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“On the Limit of the Liquid State.” By J. B. HANNAY, F.R.S.E., &c. Communicated by Professor G. G. STOKES, LL.D., D.C.L., &c., Sec. R.S. Received February 22, 1881. Read March 10, 1881.

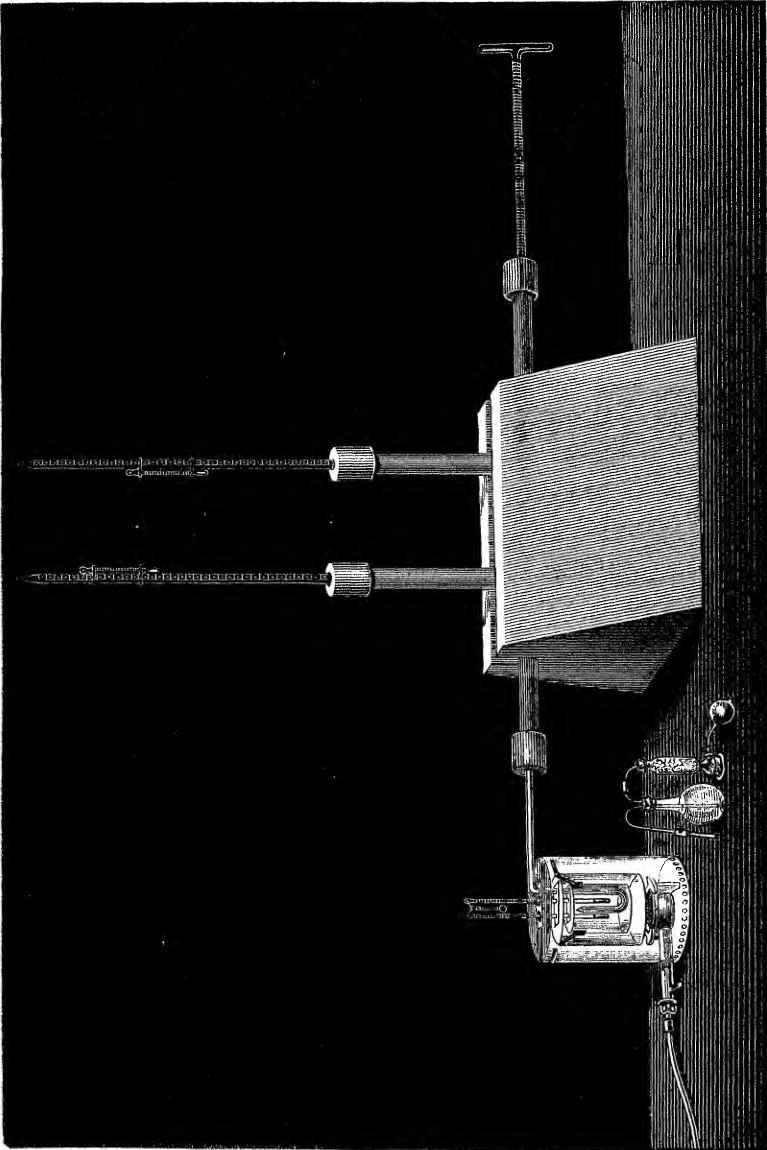
The uncertainty which characterises our knowledge of the true condition of a fluid immediately above and below the critical temperature, induced me to enter into a full examination of various fluids, with the object of gaining accurate definitions of the liquid and gaseous states, as well as to arrive at a true conception of the state of matter to which the term vapour can be applied. In a former paper, which the Royal Society has honoured me by publishing,* experiments were detailed which seemed to show that the liquid state terminated at the critical temperature, and that no amount of pressure would suffice at any higher temperature to render the fluid capable of exhibiting

* “On the State of Fluids at their Critical Temperatures.” “Proc. Roy. Soc.,” vol. 30, p. 484.

surface tension or capillarity; in fact, that the state of a fluid above that temperature coincided with the properties we call gaseous. The paper concluded, "The difference between the liquid and the gaseous states is not then entirely dependent upon the length of the mean free path; but also upon the mean velocity of the molecule." That is to say, we may compress a gas (when a few degrees above the critical temperature) to a less volume than it might occupy as a liquid, and it will still remain gaseous. In the following paper, therefore, the term liquid will be applied only to such bodies as exhibit surface tension, either as capillarity or by forming a permanent limiting surface when in contact with a vapour or gas. The term gas will be applied to that state of a fluid which precludes its being reduced to a liquid by pressure alone, in other words, to any fluid above its critical temperature. The term vapour will be applied, as has already been done by Andrews, to fluids which can be reduced to liquid by pressure alone, that is, to any æriform fluid at a temperature lower than the critical. Thus carbon dioxide is a vapour at ordinary temperature, but is a gas at temperatures over 31° . A further distinction of gas and vapour lies in the fact that, on increasing the pressure, the volume of a gas goes on diminishing in a regular way, whereas there is a part of the curve representing pressure and volume of vapour where the curve is asymptotic, that is, where the vapour is in contact with its liquid.

In the following paper reasons will be shown for believing that the gaseous state depends entirely upon the mean velocity and not upon the mean free path of the molecule at all. The difference between vapour and liquid, on the other hand, is entirely one of the length of the mean free path. The methods of experiments used were similar to those detailed in the paper above referred to, but a larger apparatus was employed, so that the results might be more distinctly visible. It was soon noticed that the readings of pressures of manometers varied a little with the diameter of the tube employed, the smallest bore giving the highest reading, and this was the case to such an extent as to cause an error of two atmospheres in 70, and about five in 100; the higher the pressure the greater the difference. The wide tube was about 0.8 millim. in diameter, the smaller 0.1 millim. Now, whether this error was caused by the hydrogen condensing against the glass, and being thus lost as a manometric substance, or whether it was caused by the hydrogen being dissolved in the film of moisture which may be supposed to adhere to the interior of the tube, has not yet been determined. It has been shown by Professors Liveing and Dewar that the moisture adhering to glass is not driven off till nearly a red heat is reached, and we may be sure that the capillarity of the smaller tube would cause it to retain moisture more eagerly than the larger one. Whatever was the cause, it was almost invariably found that manometers with small bores gave higher read-

FIG. 1.



ings than those with wide bores. They were dried by passing dried hydrogen through them for over two hours and keeping them warm all the time.

In order to obtain readings which would always be near the truth, and be more independent of accidental errors, an apparatus was constructed with two manometer tubes, and the manometers were made of tubes as wide as was consistent with the strain they were destined to bear. The apparatus as used is shown in fig. 1, where the two manometers are shown fixed in the two upright branches, while the pressure screw is at the right hand, and the working tube at the left. The air-bath has been drawn as though it were transparent, to show the internal arrangement. The working tube is recurved, so that the liquid to be experimented upon is contained between the mercury and the sealed top of the tube. The air-bath consists of two cylindrical baths with holes in the lids for passing the working tube through, and an outside cover which keeps the heat from the lamp from being too quickly radiated. The internal baths are supported by one of Fletcher's solid flame burners, and the bottoms are covered by a layer of non-conducting cement. The outside cover has openings at the top for the escape of the burnt gases, and its top is covered with a thick layer of asbestos wool, to prevent cooling. The whole of the baths and cover were made of iron, as the high temperature used caused copper to scale heavily.

Two thermometers were used in the bath, one on each side of the working tube; and at first each thermometer had a little one fixed to it for temperature corrections, but it was subsequently found that one hung between the two gave quite as much accuracy.

The two thermometers used were of soda-glass with cylindrical bore, and registered the same temperatures to within $0^{\circ}.5$, being chosen from a number. They were heated and cooled from 270° to 0° over seventy times, and one sent to Kew, where it was compared with the standard up to 100, and the stem calibrated and the corrections up to 350 calculated. The zero points of both thermometers rose from $0^{\circ}.2$ to $2^{\circ}.2$ during the preliminary heating and cooling. The changes were determined daily. The temperatures given in this paper may, therefore, be considered practically correct.

Two small thermometers were fixed to the manometers for temperature corrections.

After trying several stands I found that shown in fig. 1 to be the most convenient and steady; it is simply a large block of wood with a groove cut in it, in which the tube lies, the two upright arms preventing any movement of the apparatus. The packing of the joints has been described before, and I would only add that I find it better to face the India-rubber packing with leather by fixing a piece of fine soft leather to the face of the plug with india-rubber solution.

This leather face is then oiled, and can be screwed up with much less damage to the india-rubber plug. The larger the screw the more easily is it kept tight. The first screw I used was $\frac{3}{16}$ of an inch, and it soon cut the leather facings; the second was $\frac{5}{16}$, and it was found to last much longer; and now working with a half-inch screw it has not required repacking for three months, although in constant use. The dimensions of the apparatus as used are as follows:—Length of horizontal tube, 24 inches; height of vertical branches, 8 inches; caps, 2 inches long by $1\frac{3}{4}$ inches diameter; screw, $\frac{1}{2}$ inch; external diameter of tube, $1\frac{1}{3}$ inches; internal diameter, $\frac{5}{8}$ inch; length of manometers, 22 inches to 26 inches; external diameter, $\frac{1}{4}$ inch to $\frac{3}{8}$ inch; internal diameter, from $\frac{1}{16}$ inch up to $\frac{1}{8}$ inch. Small bath, 5 inches high by 4 inches diameter; larger bath, 7 inches by 6 inches; external cover, 13 inches high by 9 inches diameter. In each of the baths and in the cover two vertical slits were cut and fitted with mica windows, and a light placed behind allowed an observer to see clearly what occurred. The measurements are given in English standards, as engineers who construct such apparatus always use that method of measurement.

As Amagat has shown that hydrogen is the only gas which follows Boyle's law at high pressure, that gas was always used as the manometric substance, and was carefully purified and dried before use. The drying was done by passing it through five U-tubes with pumice-stone and strong sulphuric acid, and then through two U-tubes with phosphoric anhydride. The manometers used were always 0.4 millim. in internal diameter, as narrower manometers always gave higher readings. In determining the pressure of alcohol at its critical temperature, the difference of pressure indicated by different manometers puzzled me at first, especially as there was no difference in temperature, but upon determining the diameters of the manometer tubes it was found that the highest pressures were registered by the smallest bores.

The pressure of alcohol at its critical point as registered by the different manometers was as follows:—

Temperature (theory).		Diameter in millims.		Pressure in atmospheres.
232.14		0.142		69.7
232.07		0.272		69.1
232.12		A 0.480		68.1
231.99		B 0.628		67.9

These numbers are the means of thirty measurements in each case. The manometers A and B were used in most of the first portion of the work, but as they both broke subsequently, they were replaced by two others, A' and B', and these again by A'' and B''. When a pressure of

over 300 atmospheres is required, these wide manometers are very apt to burst, so that for high pressures a narrower tube must be used.

The first work undertaken was to ascertain without doubt the critical point of pure anhydrous ethyl alcohol, and this was done as follows:—The alcohol sold as absolute by the makers was fractionated, and the middle third taken. This was placed in a retort with freshly burnt lime, and an inverted condenser adapted to it. After it had been boiling for some time, the end of the condenser was fitted with a drying tube of calcium chloride, to prevent moisture from entering. The cohobation was continued for a week, and the alcohol then distilled off. The first fifth was rejected, as was also the last. The receiver was a small flat-bottomed flask, which is shown fitted up for use (after it was filled with alcohol) in the front of the drawing. It was arranged as a wash-bottle, having the tube for the entrance of air connected with a small vitriol tower, and an india-rubber ball, fitted with valves, to apply pressure. The exit tube was adapted to the experimental tube by a piece of india-rubber tubing, through which was forced a piece of capillary tubing. When the apparatus was to be used in experiment the arrangements were made as follows:—The cap with the pressure-screw was first fitted on next the experimental tube, with its point sealed up, and the whole filled up to the top of the manometer branches with mercury. The manometers were now placed in position and screwed tight. The apparatus was then tilted so as to raise the point of the experimental tube, keeping it, however, above the level of the lower ends of the manometers, and the point then broken off. If the point were below the level of the manometers some gas might escape. The wash-bottle arrangement is then fitted to the experimental tube and the ball compressed. Alcohol is driven over and escapes by the capillary tube, and this is continued till the inside of the tube has been well washed and all impurities removed. The capillary tube is then withdrawn, when the small puncture in the india-rubber at once closes itself. The screw of the pressure apparatus is then retreated, and when sufficient alcohol is made to enter the apparatus, the joint is undone and the whole wash-bottle arrangement placed under a bell-jar over oil of vitriol for use another time, the india-rubber tube being clipped. The screw is then further retreated to leave a small air-space over the alcohol, which is then boiled and the point sealed, and the tube placed in the air-bath. A mercury regulator, such as I have described elsewhere, was sometimes used when the temperature was required to be constant for long.

The following tables contain some of the series of observations on alcohol, and are given to show the numbers obtained when the work is done with every care. The alcohol used was different in each case, so that slight variations in the averages may be due to differences in the

liquid used. The numbers for pressures are arbitrary scale readings, and are reduced to actual pressures at the end of the tables.

Table No. I.

Critical Temperatures and Pressures of Alcohol.

T and T' are the two thermometers in the bath, one on each side of the experimental tube.

t and t' two thermometers for correction of T and T'.

P and P' are the readings of the two manometers A and B.

t'' and t''' two thermometers for correction of manometers.

T.	T'.	t .	t' .		P.	P'.	t'' .	t''' .
233	234	72	84		187.2	224.5	16.5	17
232	233	75	89		187.8	224.7	17	16.8
232	234	74	85		185.9	223.4	18	17.5
235	235	75	80		188.5	225	17	16.9
230	230	82	75		185.9	223.3	18	18.2
232.5	235.5	90	85		192.4	225.7	15	15
233	234.5	88	92		191.6	225.5	15	15.5
232	230.5	85	87		186.2	224.3	15	15
232	230	90	85		187.8	224.7	16	16
232	230	92	85		187.8	224.8	16.5	16.2
231	234	85	67		187.8	224.7	16.2	16.5
235	234.5	69	85		181.5	223.5	17.5	17
234	234	92	72		187.2	224.5	17.3	17
232.5	232.5	90	84		188.5	224.8	18.2	18
236	237	86	90		188	224.7	16.5	16.2
233	232	80	84		186.9	224	15.5	15.3
235	236	92	78		187.2	224.5	14.5	15
231	232	84	90		185.2	224.1	15.5	15.8
230	231	82	84		193.6	225.9	16.8	16.5
230.5	232	94	82		184	225.8	16.2	16
230.8	229.5	85	80		187	224.5	16	16
231.5	234	82	85		186.1	224.3	15	15
233.5	232.5	90	87		185.4	224.2	17	16.8
234	234	90	89		196.7	226.5	17.3	17.2
233	230	85	85		196.3	226.4	16.8	16.6
233	234	62	72		189.4	225	20.5	20
233	232	65	60		189.6	225	18.7	19
232	231	86	68		188.5	224.8	19.2	19
229	231	72	65		186.8	224.4	18.5	18.5
230	231.5	60	65		186.6	224.4	17.5	17
229	230.5	68	65		186	224.2	16	16
231	230	69	69		187.2	224.5	15.5	15

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.
233	231	75	74		181·5	223·5	14·9	15·5
231	230	72	73		181·7	223·6	16·2	17·2
230	231·5	79	84		185·2	224·3	15	15·5
229	229	92	80		184·8	224·2	16·2	17·2
230	230·5	87	85		187·8	224·8	18·5	16·7
231	231	75	82		187·7	225	17·2	18·5
231·5	231·5	85	90		185·2	224·8	19	16
232	232·5	80	80		182·7	224·2	15	15·9

Portion of thermometer scale exposed, 80° to 232°

Average T 231°·97 }
 „ T' 232°·21 } Corrected average 235°·67.

Height of mercury in manometer above tube P = 0·91 atmos.

„ „ „ „ P' = 1·14 „

Average P 187·36 } pressure in atmos. Corrected { 67·14 }
 „ P' 224·82 } { 67·98 } 67·56 atmos.

Probable error of mean temperature 0°·19.

„ „ pressure 0·13.

Table II.

Critical Point of Alcohol continued.

Manometers A' and B'.

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.
231·5	232	82	78		288	143	19	18·5
232	231	80	82		287	140	20	19·5
233	233	78	75		289	145	19	20
233·2	233·5	79	76		288	144	20	20
233	233	80	85		287	140	21	21
232	232·5	81	79		290	148	20	20
233	233	82	81		287	140	20	19
231	229	79	84		290	147	19	18·5
231	229	80	72		288	143	16	17
231	229	79	78		287	140	16	16·5
230	230	78	85		287	140	17·5	16
231·5	231	82	92		286·5	140	17	17
231	231·5	81	88		287	140·5	16·5	16·5
231·5	232	85	77		288	144	15	15·5
231·7	231·7	84	80		287	141	16	16
232	232·5	75	81		289	143	17	16·5
232	232	78	78		290	148	18·5	18
232·2	232	79	79		290	149	18·5	18

T.	T'.	t.	t'.		P.	P'.	t''.	t'''
231·8	231·5	80	85		288	147	18	18
231·8	232	82	79		287	142	17	17
231·5	232·2	81	80		288	144	16	16
232·2	232·2	80	80		288·5	145	16·5	16
232	232	80	81		287	142	16·5	17
232·2	232·5	81	80		287	140	17	17
232	232	85	81		285	138	16·5	18
232·2	232·2	76	80		287	142	15·5	16
232	232	77	78		285	138	15	15
231·8	232·2	75	76		288	145	14·5	14·5
232	232	80	79		287	142	15·5	15
232	232	78	80		287	143	15	15

Portion of thermometer exposed, 82° to 232°.

Average of T 231°·87 } Corrected mean temperature, 235°·43.
 „ T' 231°·85 }

Height of mercury in manometer above experimental tube—

Average P 287·66 } Corrected mean pressure { 66·90 } 66·88.
 „ P' 142·17 }

Probable error of mean temperature 0°·16.

„ „ pressure 0°·09.

Table III.

Critical Temperature and Pressure of Alcohol.

Manometers A'' and B''.

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.
232	232·5	82	78		212	122·8	16	18
230	232	75	82		212·5	123·5	17	17
232	232·2	78	78		213	125	19	18
232·2	232·5	80	80		211	121	20	19
232·2	232·5	82	81		210·5	120	20·5	20·5
232	232·5	84	83		211	121	20	20
233	232	80	80		211·5	122	19	19
232	232·2	80	79		212	123	18·5	18
231·5	232·8	80	76		212·2	123·4	18·5	17
232	231·5	80	81		212·1	123·2	18·6	19
232·5	232	85	83		211·9	123	19	19
231·5	231·8	82	82		212	121	18	17
232·5	231·5	89	87		212·3	123·7	17·5	16
232	232	72	75		211·6	121·8	16·5	16·5
231·5	232·5	74	75		212·2	122·7	14·2	14

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.
234	232·5	70	76		212·5	124	14·5	15
232	232	78	77		213	125	16	16·5
231	231	79	79		211	120·5	16	16
230	229	77	80		210·5	120	15·5	15·5
231·5	230·5	75	80		211·8	121	15·5	16
232·5	232	82	80		211·7	121	15·5	16
233	231	83	82		211·3	123	16	15
232	231·5	84	83		212·1	123	16	16
232	231·8	81	80		212·0	122·8	16	16
232·5	232	85	86		212·2	123	15·5	16·5
233	232·5	80	80		211·8	122	15·5	15·5
231	231·5	80	81		212·5	122·9	17	17·5
231·5	231	79	78		212·6	123·5	19	18
229·5	230·5	75	80		212·2	123	15·5	15
231·5	232	78	80		211	121	15	15
232	231	75	74		212·2	122·8	16	15
232·5	232·5	78	78		212·5	123·9	18	17

Portion of thermometer exposed, 80° to 232°.

Average T 231°·88 } Corrected mean temperature 235°·39.
 „ T' 231°·77 }

Height of mercury in manometers over experimental tube—

Average P 211·92 } Corrected mean pressure { 66·75 } 66·78 atmos.
 „ P' 122·48 } { 66·82 }

Probable error of mean temperature 0°·10.

„ „ pressure 0·06.

We see from the foregoing tables that the mean of over a hundred experiments gives a critical point for alcohol of 235°·47 under a pressure of 67·07 atmospheres. The reason why so many experiments were done was because the first two or three series did not agree well, and it was only after some experience was gained at the work that good results were obtained. I have no doubt that by further refining of the methods better results would be obtained, but I do not think the above numbers would require material alteration. Having now fixed the critical temperature and pressure of alcohol under its own vapour, the next work consisted in determining the critical temperature of the same liquid under greater pressure. When any greater pressure than the critical is used, the tube is filled with a homogeneous fluid, the two states of a fluid being impossible under such a pressure. The critical state cannot, therefore, be observed under such conditions, as all the phenomena by which the liquid state can be recognised are dependent upon the observation of a limiting surface having a certain

contractile power, and such power cannot be observed except the liquid have a free surface—that is, a surface bounded by another fluid with which it is not miscible. It was found that all liquids such as water, hydrocarbons, ethers, &c., however immiscible they may be at ordinary temperatures, mix freely or act upon one another long before the critical point of one of them is reached; therefore liquids will not serve to furnish a free surface. A gas, therefore, is the only substance which will bear any pressure without becoming miscible; and if it is insoluble in the liquid (and all liquids have some gases insoluble in them) we are provided with a substance to overlies the liquid which will allow of a limiting surface being seen at any pressure. This was the method used. A quantity of pure dry hydrogen was placed over the alcohol, and pressure applied, and the effect of rise of temperature observed. It was seen that when the temperature rose to the critical point the line dividing the alcohol from the mixture of alcohol vapour and hydrogen became quickly indistinct, and was replaced by a broad mark, indicating a gradual change in the refractive index of the fluid when passing the place where the liquid surface had been, showing that diffusion was taking place. On lowering the temperature before much diffusion had taken place, the point where the liquid surface had been became dim just as the temperature passed below the critical temperature and the sharp limiting surface became re-established.

The pressure was then increased by decreasing the volume of hydrogen, and the experiment repeated many times at the new pressure. The temperature must be raised much more slowly for these observations than for the simple observation of the critical point with alcohol alone, as in the latter case the upper and lower portions of the fluid become of the same density, instantly obliterating the line of the meniscus; but when hydrogen is above the alcohol the line remains although the alcohol be gaseous, until it is obliterated or broadened by diffusion. Thus, on raising such a mixture to the critical temperature, it is necessary to keep the temperature steady, to ascertain whether or not diffusion will take place. If a rise of temperature is going on, the thermometers will register a higher temperature than that at which diffusion began. In this way the following series of observations were carried out:—

Table IV.

Alcohol with Hydrogen.

Manometers A'' and C.

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.
230	232	80	75		220	288	17	17
229	229	75	73		221.5	291	20	18
231	230.5	78	70		219	287	21	19

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.
234·5	229·5	77	72		219	287	18	16
234	228·5	76	80		219·5	287	19	15
232	231	73	82		219·5	287	17	15
233	232·5	82	80		217	285·5	16	16
232	232·5	78	80		220·5	288	15	15
232·2	232·5	79	74		219·8	287	14	14
231·5	232·5	62	74		215·5	282·5	15·5	15
231·5	232·5	69	69		218·8	286	16	16
233	232	74	74		220	287·5	17	17
231·5	232·2	72	73		219·5	288	16	15
232	231·5	79	79		217·5	286	17	17
232	233·5	85	82		217·5	285·5	15·5	16
233·5	232·5	87	85		212	275	16	16
232	233	82	83		219	285	17	18
232·5	232	80	78		218	284	17	17
231	231·5	76	76		219·5	287	15	15
231·5	232·5	76	74		219·8	287	16	15
232	233	75	80		221·1	288·2	17	17
231·5	232·5	75	78		223	283	19	18
229	228·5	79	80		218·8	286·5	17	17
229·5	229·5	80	80		218·9	285·5	16	16
230	229	80	80		219·2	287	16	16
231	232	77	78		218·6	286·3	16	16
231	231	78	80		218·5	286·2	17	17
230	230	79	79		219·2	286·9	15·5	15·5
229	230	76	77		219·3	287	18	17
230	229	84	82		218·8	286·5	17	17
228	228	80	80		218·7	286·5	17	16
230	220	80	79		218·8	286·6	16	16

Portion of thermometer scale exposed 82° to 232°.

Average T 231°·30 }
 „ T' 231°·16 } Corrected mean 234°·78.

Height of mercury in manometers over tube { P = 0·93 atmos.
 „ { P' = 0·87 „

Average P 218·89 } pressure in atmos. Corrected { 82·44 } 82·53 atmos.
 „ P' 286·45 } { 82·63 }

Probable error of mean temperature 0°·17.

„ „ pressure 0·08.

From this it would appear that the critical temperature, or, at least, that temperature at which the meniscus disappears, is lowered slightly

by the hydrogen gas. Further experiments were conducted to settle this point.

Table V.

Alcohol with Hydrogen, Thermometer D.

T.	T'.	t.	t'.		P.	t.
234	228	78	77		290	15
232	230	82	80		291	16
232	232	75	73		290	18
231·5	231	80	79		291	16
229	231·5	82	84		291	17
230	231	77	78		292	18
231	232	72	75		288	17
232	231	79	78		290	15·5
230	230	81	81		289	16
231	231	82	82		288	15·5
231	231	80	79		288	17
229	229	75	75		292	16
228·5	228	80	82		291	17

Average T $230^{\circ}26$ }
 „ T' $230^{\circ}84$ } Corrected mean $234^{\circ}14$

Average P 290·07. Corrected pressure 183·7 atmos.

Probable error of mean temperature $0^{\circ}34$.
 „ „ pressure 0·19.

Table VI.

Alcohol and Hydrogen.

Manometers A'' and B''.

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.
232	231	68	72		222	171	15	15
231·5	232	72	72		222·4	170·2	16	16
232·5	233	84	80		223	172	17	17
233	232·5	92	90		222	171	16	16
231	231	92	92		221·8	169·5	18	18
229	230	90	90		222	171	17·5	17·5
234	235	88	90		222·2	171·2	15·5	15·5
231	232	75	74		223	171·4	16	16

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.
230·5	230·5	75	78		222·2	170·3	15	15·5
231	232	78	78		222·2	170·2	15	15
232	232	82	80		222·4	170·2	16·5	16
232	232·5	82	82		222	170·5	17	17
232	232·5	80	80		222·2	170	18	18·5
233	233·5	77	77		221·5	170·2	18·5	18·5
232	232	78	78		221·8	169·4	19	19
231·5	231	76	76		221·9	169·8	16	17
231·5	231·5	72	74		223	170	16	16
232	231·5	82	80		222·5	171·3	15	15·5
231	231	80	79		222·7	170·6	16·5	16
232	232	75	75		222·8	170·9	17	17
233	234	76	78		222·4	171	16	16
233·5	234	75	76		222·8	170·5	16	16
232·5	232·5	74	73		222·8	171	15	15
232	232	77	77		222·6	171	15	16
232	232	72	72		223	170·8	16	15
232	232	78	78		222·4	171·8	15·5	15
232	232·5	78	79		222·2	170·7	15·5	15
232·2	232·7	79	80		222	170	17	17
232·8	232·2	78	80		222·4	169·8	16·5	17
231·5	232	77	78		222·8	170·5	17	17
231·7	231·5	77	75		222·4	170·9	16	17
231·5	231	80	79		222·5	170·4	15·5	16
232	232	81	82		223	170·6	15	15
233	233	80	80		223·1	170·8	16·5	15·5
233·5	233·5	79	79		223	171·9	17	16
231	231·5	78	78		222·4	171·7	18	17·5
230·5	230·5	80	81		222·2	170·5	18	18
230·5	231	81	80		222	170·2	17	17
232	232	85	85		222·7	170·8	18	17·5
232·5	233	80	80		222·5	170·5	17	17
232	231·5	75	78		222·6	171·3	16	17
234	233	79	78		222·8	171·5	18	18
231·5	232	80	78		222·4	172	17·5	17

Average T 232°·16 }
 „ T' 232°·09 } Corrected mean 235°·68

Average P 222·44 }
 „ P' 170·74 } Corrected mean 122·72 atmos.

Probable error of mean temperature 0°·09.
 „ „ pressure 0·10.

Table VII.

Alcohol with Hydrogen.

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.
230	231	75	76		226	191	16	16
230·5	231	80	82		227	192	17	17
231·5	232	82	80		226·6	191·4	15	15
232	232	92	90		226·4	191·6	15	15
233	231	85	85		226·4	191·2	15	15
232·5	233	90	92		226·5	191	15	15·5
232	231	82	80		226·2	192·2	15·5	16
229	230·5	78	77		227	191·8	16	16
230·5	230	76	76		226·8	192	16	16·5
231·5	231·5	77	77		227	191·4	15·5	15·5
232	230	82	82		226·2	191	16	16
231·8	232	80	82		226	191·2	17	17
230·4	232	73	72		226·4	191·4	18	17·5
232·5	231·3	72	75		226·6	191·3	17	17
231	232	80	80		226·9	192·1	15	15

Average T 231°·35 }
 „ T' 231°·61 } Corrected mean 235°·04.

Average P 226·58 }
 „ P' 191·55 } Corrected mean 178·80 atmos.

Probable error of mean temperature 0°·18.
 „ „ pressure 0·07.

From these tables we see clearly that the critical temperature is not materially altered by a very large increase of pressure; in fact, in the last case the pressure is nearly three times as great, and yet we have only a lowering of the critical temperature by about one degree. It was found, however, that as the pressure was increased the solubility of the hydrogen in the alcohol also increased, so that at high pressures a very considerable lowering of the critical temperature takes place. When the two fluids have thoroughly mixed at a temperature over the critical point, the passage of the mixture through the critical temperature downwards is not attended with immediate liquefaction; in fact, this does not take place till a temperature 10° lower is reached, the hydrogen preventing the alcohol from assuming the liquid condition. At a pressure of 250 atmospheres the meniscus disappeared, or rather became broad at 225°; but diffusion did not take place completely; the surface seemed to be destroyed, but the action did not go deeper, while at 300 atmospheres the meniscus was lost at 220°. This is plainly owing to the action of the compressed hydrogen, and could we have a gas quite insoluble in the liquid, this lowering would not take

place. It seems clear then that the temperature at which the permanent surface of a fluid (which constitutes liquidness) disappears is not altered by increase of pressure, and this is equivalent to saying that the critical point is the termination of an isothermal line which marks the limit of the liquid state.

It next remained to be seen whether any other insoluble gas would act in the same manner as hydrogen. It must be remembered that hydrogen is furthest removed from the liquid condition and the least dense body known, and the nearer the density of the superincumbent gas approaches to the density of the liquid, the greater effect will it have upon the critical temperature. To test this, a quantity of nitrogen was placed over alcohol, and the experiment conducted similarly to those with hydrogen.

Table VIII.
Alcohol with Nitrogen.
Manometer C.

T.	T'.	t.	t'.		P.	t''.
231.5	232	78	79		274	16
232	231.5	77	77		267	16
231.5	231.5	78	78		262	15.5
232.5	232	80	81		262	15
232	231.5	82	80		270	15
231.5	232	80	80		270	15
232.5	232	81	81		276	16
230	231	80	82		276	17
229	230	80	78		276	18
231.5	232	75	74		278	17
231.5	231.5	76	78		277	16
232.5	232	78	80		273	15

Average T 231°50 }
 „ T' 231°58 } Corrected mean temperature 235°11.

Average P 271.75. Corrected mean pressure 82.35 atmos.

Probable error of mean temperature 0°22.

„ „ pressure 0.19.

These numbers plainly show that the meniscus of alcohol disappears at the same temperature, whether under the pressure of its own vapour or at a pressure of eighty atmospheres with nitrogen, affording further proof that the liquid state terminates at the critical temperature.

Another method still remained to be tried, that of measuring the capillary height of a liquid under various pressures and temperatures. The method used at first was to fix a small piece of capillary tubing

into the interior of the working tube by melting a small piece of silicate of soda, and causing the tube to adhere; but this was found to be disadvantageous, as the tube almost invariably burst where the silicate was adhering. The method latterly used was simply to make an obtuse-angled bend on the tube, so that the piece of capillary tube could not pass beyond this, but became wedged. The capillary height was measured by a cathetometer in the usual manner.

The following table gives the results:—

Table IX.
Capillary Height of Alcohol.
Manometers A'' and B''.

T.	T'.	t.	t'.		P.	P'.	t''.	t'''.	Cap. Ht.
10·5	10·5	..	..		..	..	..	..	564
19	19	16	16		..	..	..	..	557
34	34	16	15·5		..	..	..	..	540
54	53·8	15·5	15·5		..	..	..	..	513
67	67	15	15		..	..	..	..	487
81	80·5	16	16		..	..	..	..	468
90	90·2	17	17		..	..	..	..	450
108	108	16	16		..	..	..	..	428
122	122	18	17		..	..	..	..	402
127	127	18	18		..	..	..	..	388
137	136·5	20·5	20		..	..	}		374
145	145	23	23		80	..			358
155	154·2	27	27		92	..	16		334
166·5	166·5	35	34		112	..	16·5		300
172	173	42	40		137·5	..	17		264
186	186	53	50		165	..	17		238
192	193	60	60		185	..	16·5		211
195	195	60	61		189·5	27	16·5		194
202	202	65	66		199	52	16·5		179
205	205·5	70	72		204	83	16		161
209	210	70	70		206	90	15·5		141
214	214	72	75		208·5	107	15		127
220	220·5	75	75		210	115	17		84
225	224·5	78	78		211	118·5	17		49
229	230·5	79	80		212	123	17		8

From this table curves Nos. I, fig. 2, and IX, fig. 3, have been drawn, while Table X gives the corrected values for capillary height under the pressure of alcohol vapour. The numbers expressing the pressure of the vapour at temperatures below those at which the manometers used began to register are taken from Regnault's observations.

FIG. 2.

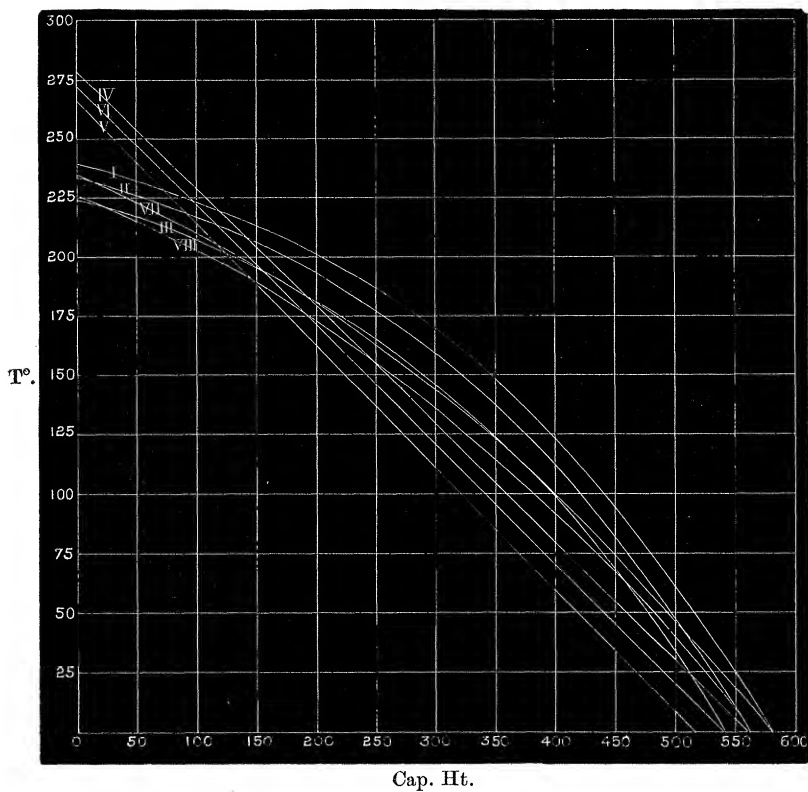


FIG. 3.

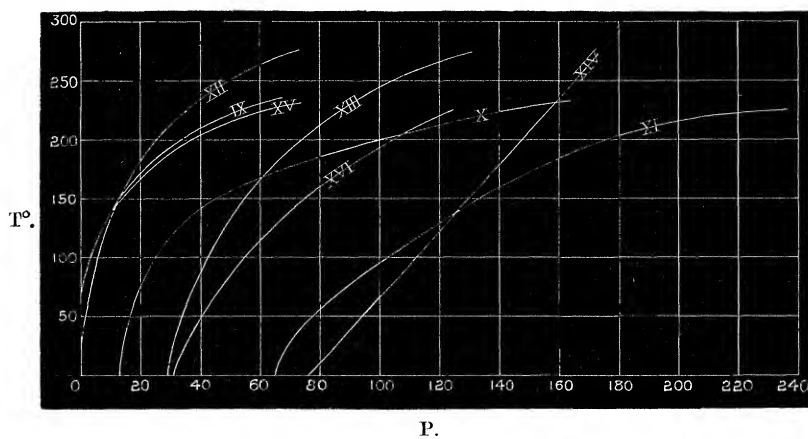


Table X.
Curves I, Fig. 2, and IX, Fig. 3.

T.	P. in atmos.	Cap. Ht.
235 ·4	66 ·7	0
230	64 ·9	40
220	58 ·7	99
200	37 ·5	198
180	18 ·1	269
160	10 ·9	321
140	7 ·4	365
	millims.	
120	3219	401
100	1694	436
80	812	467
60	350	501
40	134	530
20	44	555
0	13	579

As examples have now been given of the numbers obtained in all the different methods employed, and the probable error calculated, the tables of original numbers will be omitted and only the corrected values given, and where several observations have been made the probable error will be given.

The following table gives the capillary heights of alcohol at various temperatures under compressed hydrogen, giving a much higher pressure than the vapour alone.

Table XI.
Curves II, Fig. 2, and X, Fig. 3.
Alcohol Capillarity under Pressure.

T.	P in atmos.	Cap. Ht.
230 ·3	163 ·5	0
220	125 ·0	63
200	106 ·0	159
180	79 ·0	234
160	53 ·5	286
140	37 ·0	333
120	27 ·8	372
100	24 ·3	409
80	22 ·1	442
60	18 ·3	473
40	16 ·7	503
20	15 ·0	531
0	14 ·2	557

Table XII.

Curves III, Fig. 2, and XI, Fig. 3.

Capillary Height of Alcohol under High Pressure.

T.	P in atmos.	Cap. Ht.
224·6	236·8	0
220	224·9	26
200	182·2	129
180	145·3	207
160	136	264
140	128·1	312
120	114	354
100	100·1	391
80	86·8	428
60	79	458
40	69·1	489
20	66	517
0	64·2	544

From these tables we see that the capillary height of the liquid is lowered by a gas under pressure impinging on its surface. Thus at 66·7 atmospheres (the critical pressure of alcohol), the capillary height falls to zero at 235°·4, at 163·5 atmospheres of pressure zero is reached at 230°·3; while at 236·8 atmospheres capillarity disappears at 224°·6. It is curious to note that, although the capillary action had ceased at these temperatures, the liquids had not assumed the gaseous state, as Tables IV, V, VI, VII, and VIII show that in no case up to a pressure of 183 atmospheres did the alcohol diffuse into the hydrogen at a temperature below 234°.

As capillarity is entirely a surface phenomenon, the surface tension of a liquid seems to be weakened by the impinging of a gas under pressure upon its surface, and this we might expect to be the case, as we can imagine a constant disturbance of the surface of the liquid, owing to the high velocity of the hydrogen molecules striking it; whereas, not being soluble to any extent, few hydrogen molecules penetrate to disturb the liquidness of the interior. It would thus appear that, under such conditions, capillarity is not a true measure of the liquidness or cohesion of a fluid, and were the pressure high enough the surface of a liquid might be made to disappear, while its interior was in a truly liquid condition. This question can be most readily settled by passing a liquid, whose surface tension has thus been caused to disappear, through a capillary tube, and observing whether increase of temperature diminishes the time of flow, for the resistance of a fluid is decreased by increase of temperature, while that of a gas is increased. The experimental realisation of such a test is difficult, but apparatus is being at present constructed for the trial.

In drawing out the above tables (which may exhibit slight irregularities) recourse was made to a large number of quite separate observations, as full series are often difficult to obtain, owing to some failure in the apparatus when it has been in use for some time at high pressures.

Hitherto only one liquid—alcohol—had been used in these experiments, so it was determined to try the same experiments with other liquids, and those chosen were carbon disulphide, carbon tetrachloride, and methyl alcohol.

The carbon disulphide was digested over sodium for some time and distilled off pure quick-lime. This gives a liquid having no offensive odour and quite colourless. It was distilled into an apparatus similar to that used for alcohol, and preserved under a bell-jar over oil of vitriol. Four sets of observations were done in order to determine the critical temperature and pressure accurately; in all 163 experiments. The results are as follows:—

Mean temperature corrected.....	277°·68.
Probable error of mean.....	0°·16.
Mean pressure corrected	78·14 atmos.
Probable error	0·07 „

The apparatus was now arranged so that the critical temperature could be observed under pressure with hydrogen with the following results:—

Mean temperature corrected.....	274°·93.
Probable error	0°·09.
Mean pressure corrected	171·54 atmos.
Probable error	0·07 „

For these numbers sixty-two experiments were done.

Nitrogen was then substituted for the hydrogen, and the experiments conducted as before. Forty-one determinations were made to obtain the following means:—

Mean temperature corrected.....	273°·12.
Probable error	0°·19.
Mean pressure corrected	141·45 atmos.
Probable error.....	0·16 „

Here we see that while the pressure of the nitrogen on the carbon disulphide is much lower, the temperature at which the meniscus disappears is also lower. This is likely owing to the greater solubility of the nitrogen in the liquid, as the density makes it approach much nearer to the density of the disulphide than hydrogen.

A third series was conducted with hydrogen, using, however, a much lower pressure:—

Mean temperature corrected.....	277°·55.
Probable error	0°·14.
Mean pressure corrected	95·86 atmos.
Probable error	0·09 „

Here we see only a very faint lowering of the critical point, only 0·2 of a degree, although the pressure has been increased twenty atmospheres. The capillary height of the disulphide under various conditions was next determined. The numbers gave as follows:—

Table XIII.

Curves IV, Fig. 2, and XII, Fig. 3.

Capillarity of Carbon Disulphide.

T.	P in atmos.	Cap. Ht.
277	78·1	0
260	58·1	45
240	43·8	74
220	33·7	114
200	25·5	155
180	19·6	197
160	14·8	236
140	10·9	277
120	7·6	316
100	4·3	359
80	2·8	397
60	1·6	437
40	0·8	476
20	—	517
0	—	558

Table XIV.

Curves V, Fig. 2, and XIV, Fig. 3.

Capillarity of Carbon Disulphide with Hydrogen.

T.	P in atmos.	Cap. Ht.
260	172·1	0
260	167·2	9
240	160	46
220	153·5	84
200	146·3	122
180	138·2	164

T.		P in atmos.		Cap. Ht.
160		131.5		203
140		124.8		242
120		117.7		278
100		110.9		317
80		103.8		358
60		96.5		394
40		90.2		434
20		83.2		473
0		78		515

Table XV.

Curves VI, Fig. 2, and XIII, Fig. 3.

Carbon Disulphide with Nitrogen.

T.		P in atmos.		Cap. Ht.
273		131		0
260		112.5		23
240		96.1		61
220		83.8		100
200		73.2		141
180		64.3		197
160		58.1		236
140		52.2		278
120		46.8		317
100		42.7		358
80		39.2		395
60		37.7		436
40		33.3		478
20		30.4		517
0		28.1		555

On examining these tables, and the curves which graphically represent them, we see that here also the capillary action of the liquid is weakened by a gas impinging upon its surface, even at low temperatures, and again we see that the capillarity is reduced to zero before the liquid is really gaseous, showing that like alcohol the surface tension of carbon disulphide is destroyed by the activity of the molecules of the gas overlying it. The curve for carbon disulphide and hydrogen, XIV, fig. 3, should not be really a straight line, but a number of accidents happened during these experiments, and the curve is made up from many readings from different manometers, that for the

middle part of the curve evidently reading a little low. The whole result agrees well with what was shown from alcohol.

The next body examined was methyl alcohol, a sample of which was carefully purified in the same manner as the ethyl alcohol, until its boiling point was constant. It was then distilled off quick-lime into the wash-bottle arrangement for use. It gave as follows:—

Mean temperature corrected.....	232°·76.
Probable error.....	0°·21.
Mean pressure corrected	72·85 atmos.
Probable error	0·12 „

These means were taken from three series, each of thirty experiments. The same experiments were then carried out with methyl alcohol and hydrogen and nitrogen, as in the case of ethyl alcohol and carbon disulphide, yielding the following results from twenty-two experiments:—

Mean temperature corrected.....	230°·14.
Probable error	0°·09.
Mean pressure corrected	128·60 atmos.
Probable error.....	0·12 „

Here we have, as before, a slight depression of the critical temperature. Experiments were then tried with higher pressure. Forty-seven gave the following means:—

Mean temperature corrected.....	227°·92.
Probable error.....	0°·10.
Mean pressure corrected	191·40 atoms.
Probable error.....	0·07 „

A still higher pressure was then applied. The means of eighteen experiments were—

Mean temperature corrected.....	225°·82.
Probable error.....	0°·26.
Mean pressure corrected	262·00 atmos.
Probable error.....	0·09 „

We have a further depression of the critical point, and as the point was determined with great difficulty we have an increase of the probable error. However, the result confirms the other experiments. The same mode of experiment was then carried out with methyl alcohol and hydrogen and nitrogen as with ethyl alcohol, with the following results.

Table XVI.

Curves VII, Fig. 2, and XV, Fig. 3.

Capillarity of Methyl Alcohol.

T.		P.		Cap. Ht.
232.7		72.8		0
230		64.8		5
220		51.2		52
200		34.8		133
180		23.2		202
160		16.4		257
140		11.9		309
120		7.1		359
100		4.2		402
80		1.9		441
60		..		477
40		..		513
20		..		545
0		..		577

Table XVII.

Curves VIII, Fig. 2, and XVI, Fig. 3.

Capillarity of Methyl Alcohol under Pressure with Hydrogen.

T.		P.		Cap. Ht.
224		123.4		0
220		119.7		27
200		104.2		106
180		90.5		179
160		79.2		237
140		69.1		287
120		61.3		336
100		55.0		283
80		48.1		423
60		42.6		458
40		38.4		493
20		33.8		527
0		29.9		557

In these experiments we see again that increase of pressure never increases the liquidness of the fluid, and never enables it to remain liquid at a temperature above the critical point.

The last liquid examined was carbon tetrachloride, and this was very carefully dried and purified by fractionation and distillation off quick-lime, the purified liquid being kept with the same precautions as were used in the other cases. It was seen, however, that the tetrachloride acted upon the mercury, forming a white crystalline body which crystallised out as the liquid cooled. It appeared to be mercuric chloride, as it dissolved in water; but whether the crystals were pure mercuric chloride or a compound of that body with some other chloride of carbon there was not sufficient obtained to determine. The critical temperature and pressure were determined with twenty different samples, using one quantity only for two or three readings, and the following numbers were obtained:—

Mean temperature corrected.....	282°·51.
Probable error.....	0°·38.
Mean pressure corrected	57·57 atmos.
Probable error.....	0·14 ,,

On attempting to obtain the critical temperature under pressure it was found that the hydrogen at once dissolved under pressure, and not only dissolved, but formed a compound with the tetrachloride. Some curious observations were made on the relation of pressure to chemical combination with this mixture. It was found that for a given temperature and pressure only a certain amount of combination would take place, leaving the excess of hydrogen overlying the tetrachloride quite free. If then more pressure were applied, the manometer would jump up say five atmospheres, and then gradually fall about four or four and a half atmospheres, and again become stable, and this would take place each time, a large portion of hydrogen disappearing for a small permanent rise of pressure. A sudden rise of temperature had somewhat the same effect, but as the temperature could not be varied so suddenly the effect was not so obvious. Several bodies were formed by the action of the hydrogen, the action being capable of being pushed so far as to form chloroform. Nitrogen was used as a pressure substance, and it answered well. The following numbers were obtained from twenty-seven experiments:—

Mean temperature corrected.....	277°·56.
Probable error	0°·29.
Mean pressure corrected	142·83 atmos.
Probable error.....	0·13 ,,

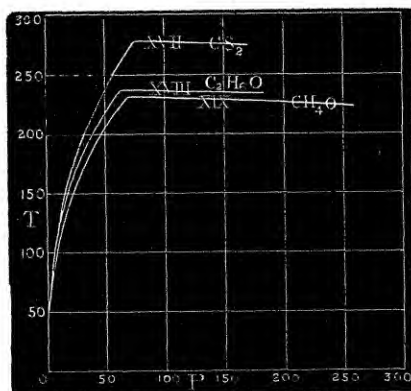
From this it will be seen that by increasing the pressure to nearly three times the normal, a fall of five degrees in the critical temperature has taken place. This was no doubt due to the surface tension being

destroyed by the action of the gaseous molecules, so another series was tried at a lower pressure. Forty-two experiments were done:—

Mean temperature corrected.....	282°·50.
Probable error	0°·12.
Mean pressure corrected	83·18 atmos.
Probable error	0·38 „

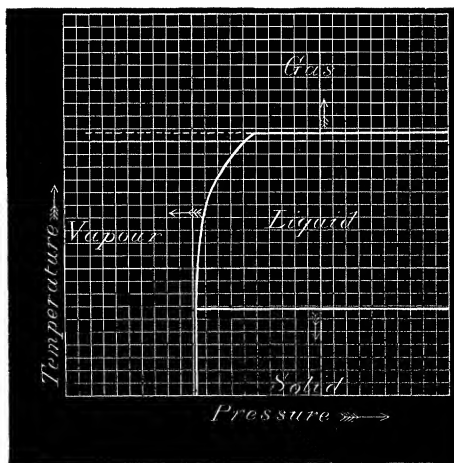
Here we see that a large increase of pressure has not altered the critical temperature at all, as was before seen to be the case with alcohol. A series of capillary measurements was commenced with this liquid, but a series of accidents interfered with the work, and only twelve reliable readings were obtained, and no time has been at my disposal since to finish the work; but sufficient evidence of the course of capillary action has already been gained from the other liquids to draw conclusions as to the liquid state and its limit.

FIG. 4.



Three curves have been drawn to show the depression of the critical temperature with increase of pressure, and these lines have been continued down the curve of vapour pressure to show the break at the critical point. This will be clearly shown in curves Nos. XVII, XVIII, and XIX, fig. 4. The consideration of these results yields a novel mode of looking at the states of matter which I have illustrated in fig. 5. From this it appears we might classify matter under four states; first, the gaseous which exists from the highest temperatures down to an isothermal passing through the critical point and depending entirely upon temperature or molecular velocity; second, the vaporous, bounded upon the upper side by the gaseous state and on the lower by absolute zero, and depending entirely upon the length of the mean free path, because shortening of the mean free path alters the state; third, the liquid bounded upon the upper side by the gaseous state, and on the lower by the solid or absolute zero; fourth, the solid

FIG. 5.



whose condition is also determined by both pressure and temperature. The gaseous state is the only one which is not affected by pressure alone, or in which the molecular velocity is so high that the collisions cause a rebound of sufficient energy to prevent grouping. Another distinction between the gaseous and vaporous states is that the former is capable of acting as a solvent of solids, whereas the latter is not.

The two conclusions arrived at from this work are—

1st. The liquid state has a limit which is an isothermal passing through the critical point.

2nd. The vaporous state can be clearly defined as a distinct state of matter.

To the original distinction between these two states given by Andrews—namely, that of condensibility—I have added another, that of solvent power. A vapour over a liquid holding a coloured solid in solution is colourless, but on passing the critical temperature the whole becomes coloured. In some cases, however, the solid is deposited and redissolved as the temperature rises, showing that the more perfectly gaseous the greater the solvent power. Andrews's distinction compels us to travel along an isotherm, mine requires high pressure; both are thus arbitrary, requiring given conditions, but this is the case with many of the other distinctions used in science.

My thanks are due to my assistant, Mr. Ewing McConechy, for his assiduous aid during the above described investigation.

FIG. 1.



FIG. 2.

T.

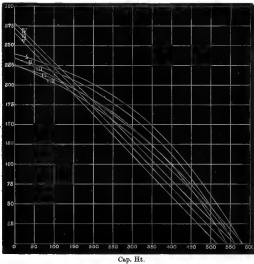


FIG. 3.

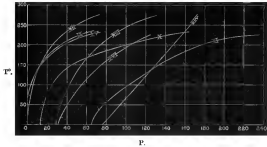


Fig. 4.

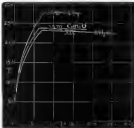


FIG. 5.

